

Supporting information

Natural small molecule-based carrier-free self-assembly library originated from traditional Chinese herb medicine

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Table S1 Identification of compounds at supramolecular sites

NO.	t _R (min)	Compound	Formula	Precursor ion			Fragment ion			
				Identity	Theoretical (m/z)	Experimental (m/z)	Δppm	(m/z)		
1	1.10	Sucrose	C ₁₂ H ₂₂ O ₁₁	[M-H] ⁻	341.1078	341.1091	3.81	179.0553	[M-H-C ₆ H ₁₀ O ₅] ⁻ , 161.0444	[M-H-C ₆ H ₁₂ O ₆] ⁻ , 113.0231
2	1.13	Glucose	C ₆ H ₁₂ O ₆	[M-H] ⁻	179.0550	179.0553	1.67	161.0446	[M-H-H ₂ O] ⁻ , 119.0335	[M-H-C ₂ H ₄ O ₂] ⁻ , 101.0231
3	1.17	Quinic acid	C ₇ H ₁₂ O ₆	[M-H] ⁻	191.0550	191.0554	2.09	173.0445	[M-H-H ₂ O] ⁻ , 127.0389	[M-H-CH ₄ O ₃] ⁻ , 93.0332
4	1.20	Ribose/ Lyxopyranose/ Xylose	C ₅ H ₁₀ O ₅	[M-H] ⁻	149.0444	149.0444	0.00	131.0337	[M-H-H ₂ O] ⁻	
5	1.22	Methyl a-D glucopyranoside	C ₇ H ₁₄ O ₆	[M-H] ⁻	193.0706	193.0710	2.07	179.0553	[M-H-CH ₂] ⁻ , 133.0495	[M-H-C ₂ H ₄ O ₂] ⁻
6	1.24	Rhamnose	C ₆ H ₁₂ O ₅	[M-H] ⁻	163.0600	163.0600	0.00	145.0494	[M-H-H ₂ O] ⁻	
7	1.35	Malic acid	C ₄ H ₆ O ₅	[M-H] ⁻	133.0131	133.0131	0.00	115.0024	[M-H-H ₂ O] ⁻ , 71.0123	[M-H-CH ₂ O ₃] ⁻
8	1.52	Citric Acid	C ₆ H ₈ O ₇	[M-H] ⁻	191.0186	191.0190	2.09	173.0080	[M-H-H ₂ O] ⁻ , 111.0074	[M-H-CH ₄ O ₄] ⁻ , 85.0280
9	2.01	Galloylglucose	C ₁₃ H ₁₆ O ₁₀	[M-H] ⁻	331.0659	331.0674	4.53	169.0132	[M-H-C ₆ H ₁₀ O ₅] ⁻ , 125.0232	[M-H-C ₇ H ₁₀ O ₇] ⁻
10	2.34	Gallic acid	C ₇ H ₆ O ₅	[M-H] ⁻	169.0131	169.0133	1.18	125.0231	[M-H-CO ₂] ⁻	
11	3.00	Gallic didextrose	C ₁₉ H ₂₆ O ₁₅	[M-H] ⁻	493.1187	493.1201	2.83	169.0134	[M-H-C ₁₂ H ₂₀ O ₁₀] ⁻ , 125.0232	[M-H-C ₁₃ H ₂₀ O ₁₂] ⁻
12	3.32	Pantothenic acid	C ₉ H ₁₇ NO ₅	[M-H] ⁻	218.1022	218.1030	3.66	116.0339	[M-H-C ₅ H ₁₀ O ₂] ⁻	
13	3.43	3-hydroxy-4-methoxybenzoic acid 3-O-β-D-glucopyranoside	C ₁₄ H ₁₈ O ₉	[M-H] ⁻	329.0867	329.0881	3.95	167.0342	[M-H-C ₆ H ₁₀ O ₅] ⁻	

14	3.99	Catechin-5-O-glucoside	C ₂₁ H ₂₄ O ₁₁	[M-H] ⁻	451.1234	451.1251	3.76	289.0717 [M-H-C ₆ H ₁₀ O ₅] ⁻ , 245.0818 [M-H-C ₇ H ₁₀ O ₇] ⁻
15	4.74	Procyanidin B	C ₃₀ H ₂₆ O ₁₂	[M-H] ⁻	577.1340	577.1359	3.29	407.0749 [M-H-C ₈ H ₁₀ O ₄] ⁻ , 289.0713 [M-H-C ₁₅ H ₁₂ O ₆] ⁻ , 245.0813 [M-H-C ₁₆ H ₁₂ O ₈] ⁻
16	4.93	3-hydroxybenzoic acid	C ₇ H ₆ O ₃	[M-H] ⁻	137.0233	137.0234	0.72	121.0283 [M-H-O] ⁻
17	5.07	1,6-Digalloyl glucopyranose	C ₂₀ H ₂₀ O ₁₄	[M-H] ⁻	483.0769	483.0787	3.72	315.0714 [M-H-C ₇ H ₄ O ₅] ⁻ , 169.0128 [M-H-C ₁₃ H ₁₄ O ₉] ⁻ , 125.0231 [M-H-C ₁₄ H ₁₄ O ₁₁] ⁻
18	5.23	Methyl gallate	C ₈ H ₈ O ₅	[M-H] ⁻	183.0287	183.0292	2.73	124.0153 [M-H-C ₂ H ₃ O ₂] ⁻
19	5.26	2,5-dihydroxybenzoic acid	C ₇ H ₆ O ₄	[M-H] ⁻	153.0182	153.0183	0.65	109.0283 [M-H-CO ₂] ⁻
20	5.27	Epi/catechin	C ₁₅ H ₁₄ O ₆	[M-H] ⁻	289.0706	289.0720	4.84	271.0615 [M-H-H ₂ O] ⁻ , 245.0818 [M-H-CO ₂] ⁻ , 227.0707 [M-H-CH ₂ O ₃] ⁻ , 203.0708 [M-H-C ₃ H ₂ O ₃] ⁻ , 187.0392 [M-H-C ₄ H ₆ O ₃] ⁻ , 179.3041 [M-H-C ₆ H ₆ O ₂] ⁻ , 165.0183 [M-H- ^{1,2} A] ⁻ , 137.0233 [M-H- ^{1,3} A] ⁻ , 125.0231 [M-H- ^{1,4} A] ⁻
21	5.33	3-O-Feruloylquinic acid	C ₁₇ H ₂₀ O ₉	[M-H] ⁻	367.1023	367.1032	2.45	193.0500 [M-H-C ₇ H ₁₀ O ₅] ⁻ , 191.0554 [M-H-C ₁₀ H ₈ O ₃] ⁻ , 173.0448 [M-H-C ₁₀ H ₁₀ O ₄] ⁻ , 149.0597 [M-H-C ₈ H ₁₀ O ₇] ⁻ , 134.0362 [M-H-C ₉ H ₁₃ O ₇] ⁻
22	6.19	Procyanidin B 3"-O-gallate	C ₃₇ H ₃₀ O ₁₆	[M-H] ⁻	729.1450	729.1473	3.24	577.1362 [M-H-C ₇ H ₄ O ₄] ⁻ , 289.0721 [M-H-C ₂₂ H ₁₆ O ₁₀] ⁻ , 245.0817 [M-H-C ₂₃ H ₁₆ O ₁₂] ⁻
23	6.46	4-O-Feruloylquinic acid	C ₁₇ H ₂₀ O ₉	[M-H] ⁻	367.1023	367.1032	2.45	193.0500 [M-H-C ₇ H ₁₀ O ₅] ⁻ , 191.0554 [M-H-C ₁₀ H ₈ O ₃] ⁻ , 173.0447 [M-H-C ₁₀ H ₁₀ O ₄] ⁻ , 149.0596 [M-H-C ₈ H ₁₀ O ₇] ⁻ , 134.0362 [M-H-C ₉ H ₁₃ O ₇] ⁻
24	6.73	cinnamoyl glucose	C ₁₅ H ₁₈ O ₇	[M-H] ⁻	309.0968	309.0968	0.00	147.0441 [M-H-C ₆ H ₁₀ O ₅] ⁻
25	7.02	Hydroxycinnamic acid	C ₉ H ₈ O ₃	[M-H] ⁻	163.0389	163.0393	2.45	174.0442 [M-H-O] ⁻ , 119.0491 [M-H-CO ₂] ⁻
26	7.14	Vanillic acid	C ₈ H ₈ O ₄	[M-H] ⁻	167.0338	167.0342	2.39	123.0440 [M-H-CO ₂] ⁻

27	7.37	Rhein glucoside	C ₂₁ H ₁₈ O ₁₁	[M-H] ⁻	445.0765	445.0775	2.25	283.0250 [M-H-C ₆ H ₁₀ O ₅] ⁻ ;239.0348 [M-H-C ₇ H ₁₀ O ₇] ⁻ ;211.0396 [M-H-C ₈ H ₁₀ O ₈] ⁻
28	7.56	Epi catechin gallate (-)-Epicatechin-3-O-gallate)	C ₂₂ H ₁₈ O ₁₀	[M-H] ⁻	441.0816	441.0831	3.40	331.0472 [M-H-C ₆ H ₆ O ₂] ⁻ ;289.0720 [M-H-C ₇ H ₄ O ₄] ⁻ ;245.0817 [M-H-C ₈ H ₄ O ₅] ⁻ ;179.0340 [M-H-C ₁₃ H ₁₀ O ₆] ⁻ ;271.0612,169.0134[M-H-C ₇ H ₆ O ₅] ⁻ ;125.0232 [M-H-C ₇ H ₆ O ₅ - ^{1,4} A] ⁻
29	7.65	Sennoside C/D	C ₄₂ H ₄₀ O ₁₉	[M-H] ⁻	847.2080	847.2097	2.00	685.1560 [M-H-C ₆ H ₁₀ O ₅] ⁻
30	7.83	Resveratrol-4'-O-(6"-galloyl)glucoside	C ₂₇ H ₂₆ O ₁₂	[M-H] ⁻	541.1340	541.1356	2.96	313.0568 [M-H-C ₁₄ H ₁₂ O ₃] ⁻ ;227.0711 [M-H-C ₁₃ H ₁₄ O ₉] ⁻ ;169.0134 [M-H-C ₂₀ H ₂₀ O ₇] ⁻ ;151.0027 [M-H-C ₂₀ H ₂₂ O ₈] ⁻
31	7.85	Sennoside A/B	C ₄₂ H ₃₈ O ₂₀	[M-H] ⁻	861.1872	861.1890	2.09	699.1338 [M-H-C ₆ H ₁₀ O ₅] ⁻ ;386.0994 [M-H-C ₂₂ H ₁₉ O ₁₂] ⁻
32	8.40	Resveratrol	C ₁₄ H ₁₂ O ₃	[M-H] ⁻	229.0859	229.0868	3.92	143.0492 [M-H-C ₄ H ₄ O ₂] ⁻
33	8.56	Rhein 1-O-(6'-O-acetyl)-glucoside	C ₂₃ H ₂₀ O ₁₂	[M-H] ⁻	487.0871	487.0885	2.87	283.0249 [M-H-C ₈ H ₁₂ O ₆] ⁻ ;239.0344 [M-H-C ₉ H ₁₂ O ₈] ⁻
34	8.57	Azelaic acid	C ₉ H ₁₆ O ₄	[M-H] ⁻	187.0964	187.0968	2.13	143.1066 [M-H-CO ₂] ⁻ ;121.0283 [M-H-C ₅ H ₆ O] ⁻
35	8.70	Aloesin	C ₁₉ H ₂₂ O ₉	[M-H] ⁻	393.1180	393.1196	4.07	231.0658 [M-H-C ₆ H ₁₀ O ₅] ⁻ ;203.0709 [M-H-C ₇ H ₁₀ O ₆] ⁻
36	8.86	Aloeemodin glucoside	C ₂₁ H ₂₀ O ₁₁	[M-H] ⁻	431.0972	431.0984	2.78	269.0456 [M-H-C ₆ H ₁₀ O ₅] ⁻
37	8.97	2-Cinnamoyl-1-galloylglucose (2-O-Cinnamoyl-Glucogallin)	C ₂₂ H ₂₂ O ₁₁	[M-H] ⁻	461.1078	461.1094	3.46	313.0568 [M-H-C ₉ H ₈ O ₂] ⁻ ;169.0133 [M-H-C ₁₅ H ₁₆ O ₆] ⁻ ;151.0026 [M-H-C ₁₅ H ₁₈ O ₇] ⁻ ;147.0441 [M-H-C ₁₃ H ₁₄ O ₉] ⁻
38	10.05	2-O-Cinnamoyl-1,6-O-galloylglucose	C ₂₉ H ₂₆ O ₁₅	[M-H] ⁻	613.1187	613.1206	3.09	465.0655 [M-H-C ₉ H ₈ O ₂] ⁻ ;313.0558 [M-H-C ₁₆ H ₁₂ O ₆] ⁻ ;169.0138 [M-H-C ₂₂ H ₂₀ O ₁₀] ⁻
39	10.21	Torachryson	C ₁₄ H ₁₄ O ₄	[M-H] ⁻	245.0808	245.0815	2.85	230.0566 [M-H-CH ₃] ⁻ ;187.0394 [M-H-C ₃ H ₆ O] ⁻

40	10.22	Torachryson 8-O-glucoside	C ₂₀ H ₂₄ O ₉	[M-H] ⁻	407.1336	407.1350	3.43	245.0817 [M-H-C ₆ H ₁₀ O ₅] ⁻ ,230.0580 [M-H-C ₇ H ₁₃ O ₅] ⁻
41	10.24	Isovitexin	C ₂₁ H ₂₀ O ₁₀	[M-H] ⁻	431.0972	431.0987	3.47	268.0378 [M-H-C ₆ H ₁₁ O ₅] ⁻
42	10.27	Chrysin	C ₁₅ H ₁₀ O ₄	[M-H] ⁻	253.0495	253.0505	3.95	225.0555 [M-H-CO] ⁻
43	10.28	Chrysophan-1-O-glucoside	C ₂₁ H ₂₀ O ₉	[M-H] ⁻	415.1023	415.1037	3.37	253.0505 [M-H-C ₆ H ₁₀ O ₅] ⁻ ,225.0555 [M-H-C ₇ H ₁₀ O ₆] ⁻
44	10.30	emodin glucoside	C ₂₁ H ₂₀ O ₁₁	[M-H] ⁻	431.0972	431.0984	2.78	269.0456 [M-H-C ₆ H ₁₀ O ₅] ⁻
45	10.32	Aloe-Emodin 8-O-(6'-O-acetyl)- glucoside	C ₂₃ H ₂₂ O ₁₁	[M-H] ⁻	473.1078	473.1090	2.53	268.0369 [M-H-C ₈ H ₁₃ O ₆] ⁻ ,224.0464 [M-H-C ₉ H ₁₃ O ₈] ⁻
46	10.35	Iso/Lindleyin	C ₂₃ H ₂₆ O ₁₁	[M-H] ⁻	477.1391	477.1392	0.20	169.0135 [M-H-C ₁₆ H ₂₀ O ₆] ⁻ ,125.0231 [M-H-C ₁₇ H ₂₀ O ₈] ⁻
47	10.49	Chrysophan-8-O-ol glucoside	C ₂₁ H ₂₀ O ₉	[M-H] ⁻	415.1023	415.1037	3.37	253.0506 [M-H-C ₆ H ₁₀ O ₅] ⁻ ,225.0553 [M-H-C ₇ H ₁₀ O ₆] ⁻
48	10.50	Chrysophanol	C ₁₅ H ₁₀ O ₄	[M-H] ⁻	253.0495	253.0506	4.35	225.0555 [M-H-CO] ⁻
49	10.51	8-O-Methyl Chrysophanol	C ₁₆ H ₁₂ O ₄	[M-H] ⁻	267.0651	267.0657	2.24	252.0423 [M-H-CH ₃] ⁻ ,238.0632 [M-H-C ₂ H ₅] ⁻
50	10.77	Endocrocin	C ₁₆ H ₁₀ O ₇	[M-H] ⁻	313.0342	313.0355	4.15	269.0456 [M-H-CO ₂] ⁻ ,241.0501 [M-H-C ₂ O ₃] ⁻ ,225.0551 [M-H-C ₃ O ₅] ⁻
51	11.09	Torachryson 8-O-(6'-O-acetyl)- glucoside	C ₂₂ H ₂₆ O ₁₀	[M-H] ⁻	449.1442	449.1458	1.33	245.0815 [M-H-C ₈ H ₁₂ O ₆] ⁻ ,230.0573 [M-H-C ₉ H ₁₅ O ₆] ⁻ , 215.0335 [M-H-C ₁₀ H ₁₈ O ₆] ⁻ ,183.0398 [M-H-C ₁₁ H ₁₈ O ₇] ⁻
52	11.18	Wogonin (oroxylin A)	C ₁₆ H ₁₂ O ₅	[M-H] ⁻	283.0600	283.0612	4.24	268.0377 [M-H-CH ₃] ⁻ ,240.0425 [M-H-C ₂ H ₅ O] ⁻
53	11.20	Emodin 8-O-(6'-O-acetyl)- glucoside	C ₂₃ H ₂₂ O ₁₁	[M-H] ⁻	473.1078	473.1093	3.17	268.0378 [M-H-C ₈ H ₁₃ O ₆] ⁻ ,240.0410 [M-H-C ₉ H ₁₃ O ₇] ⁻
54	11.42	Physcion	C ₁₆ H ₁₂ O ₅	[M-H] ⁻	283.0600	283.0612	4.24	268.0377 [M-H-CH ₃] ⁻ ,240.0425 [M-H-C ₂ H ₅ O] ⁻

55	11.47	Physcion glucoside	C ₂₂ H ₂₂ O ₁₀	[M-H] ⁻	445.1129	445.1139	2.25	283.0612 [M-H-C ₆ H ₁₀ O ₅] ⁻ ;268.0377 [M-H-C ₇ H ₁₃ O ₅] ⁻ ;240.0425 [M-H-C ₈ H ₁₃ O ₆] ⁻
56	11.53	Chrysophanol 1-O-(6'-O-acetyl)- glucoside3-methyl- Rhein	C ₂₃ H ₂₂ O ₁₀	[M-H] ⁻	457.1129	457.1151	4.81	253.0505 [M-H-C ₈ H ₁₂ O ₆] ⁻ ;239.0710 [M-H-C ₉ H ₁₄ O ₆] ⁻
57	11.55	Naringenin	C ₁₅ H ₁₂ O ₅	[M-H] ⁻	271.0600	271.0613	4.79	177.0184 [M-H-C ₆ H ₄ O] ⁻ ;165.0183, 107.0126 [M-H- ^{1,2} C] ⁻ 151.0026, 119.0490 [M-H- ^{1,3} C] ⁻ ;93.0332 [M-H-C ₉ H ₆ O ₄] ⁻
58	12.33	Calycosin	C ₁₆ H ₁₁ O ₅	[M-H] ⁻	283.0600	283.0613	4.59	268.0378 [M-H-CH ₃] ⁻ ;240.0425 [M-H-C ₂ H ₃ O] ⁻ ;212.0472 [M-H-C ₃ H ₃ O ₂] ⁻
59	12.34	Physcion 8-O(6'-O-acetyl)gl ucoside	C ₂₄ H ₂₄ O ₁₁	[M-H] ⁻	487.1234	487.1248	2.87	283.0613 [M-H-C ₈ H ₁₂ O ₆] ⁻ ;268.0370 [M-H-C ₉ H ₁₅ O ₆] ⁻ 240.0408 [M-H-C ₁₀ H ₁₅ O ₇] ⁻
60	12.80	3-methyl-Rhein	C ₁₆ H ₁₀ O ₆	[M-H] ⁻	297.0393	297.0406	4.37	253.0505 [M-H-CO ₂] ⁻ ;225.0553 [M-H-C ₂ O ₃] ⁻
61	13.82	Aloe-emodin	C ₁₅ H ₁₀ O ₅	[M-H] ⁻	269.0444	269.0456	4.46	241.0498 [M-H-CO] ⁻ ;240.0426 [M-H-CHO] ⁻ ;223.0397 [M-H-CH ₂ O ₂] ⁻ 197.0597 [M-H-C ₂ O ₃] ⁻ ;183.0449 [M-H-C ₃ H ₂ O ₃] ⁻
62	14.17	1,8-Dihydroxyanth raquinone	C ₁₄ H ₈ O ₄	[M-H] ⁻	239.0338	239.0347	3.76	211.0396 [M-H-CO] ⁻ ;183.0444 [M-H-C ₂ O ₂] ⁻
63	14.23	Rhein	C ₁₅ H ₈ O ₆	[M-H] ⁻	283.0237	283.0249	4.24	239.0347 [M-H-CO ₂] ⁻ ;211.0394 [M-H-C ₂ O ₃] ⁻ ;183.0443 [M-H-C ₃ O ₄] ⁻ 155.0492 [M-H-C ₄ O ₅] ⁻

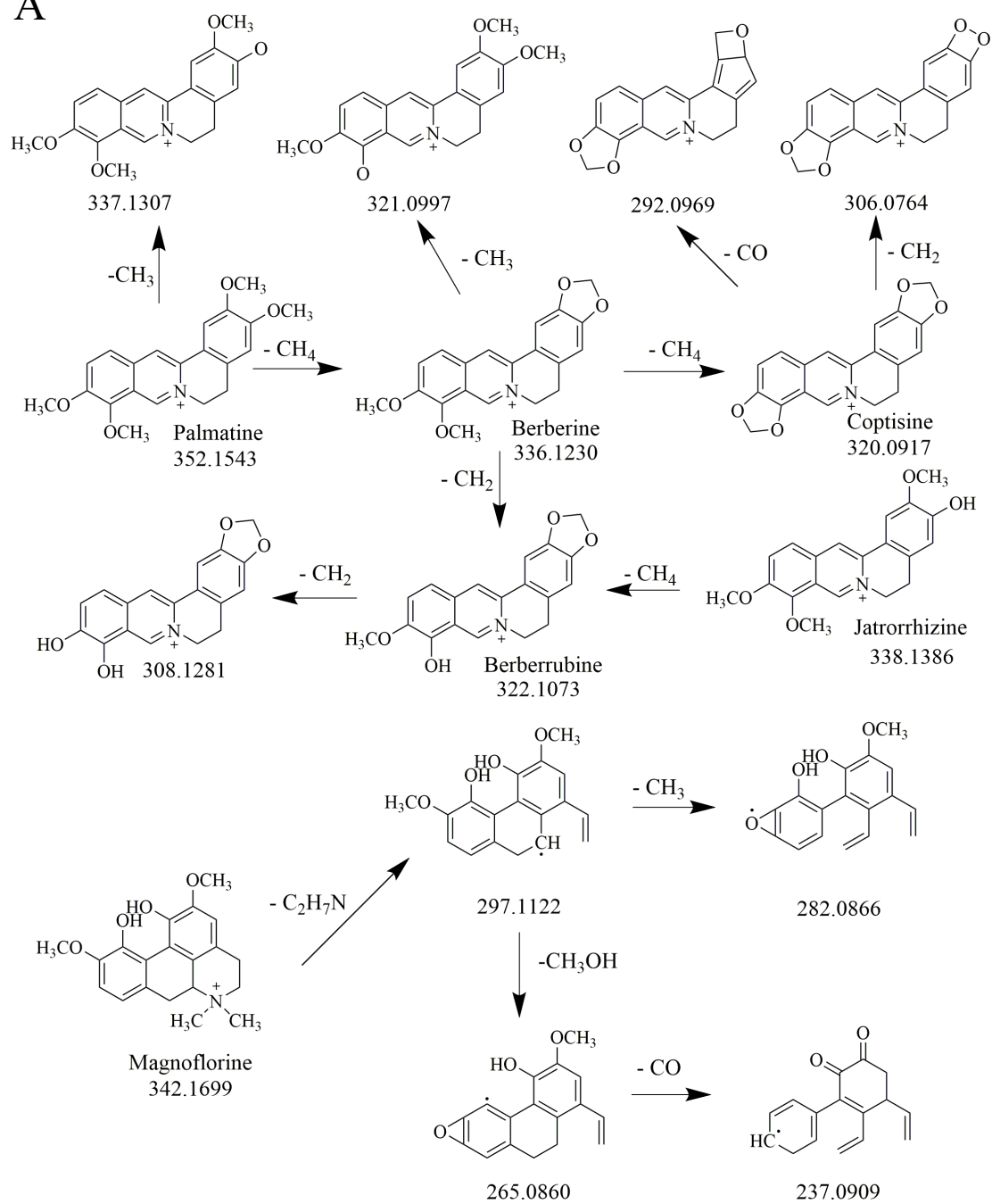
64	16.20	(4,5-Dihydroxy-9,10-dioxo-9,10-dihydro-2-anthracenyl)methyl acetate	C ₁₇ H ₁₂ O ₆	[M-H] ⁻	311.0550	311.0564	4.50	283.0610 [M-H-CO] ⁻ , 267.0658 [M-H-CO ₂] ⁻ , 240.0422 [M-H-C ₃ H ₃ O ₂] ⁻
65	17.14	Emodin	C ₁₅ H ₁₀ O ₅	[M-H] ⁻	269.0444	269.0456	4.46	241.0502 [M-H-CO] ⁻ , 225.0552 [M-H-CO ₂] ⁻ , 197.0601 [M-H-C ₂ O ₃] ⁻ , 181.0648 [M-H-C ₂ O ₄] ⁻
66	17.27	Norwogonin	C ₁₅ H ₁₀ O ₅	[M-H] ⁻	269.0444	269.0456	4.46	241.0501 [M-H-CO] ⁻ , 225.0553 [M-H-CO ₂] ⁻
67	1.13	Arginine	C ₆ H ₁₄ N ₄ O ₂	[M+H] ⁺	175.1189	175.1191	1.14	116.0710 [M+H-CH ₅ N ₃] ⁺
68	1.15	Choline	C ₅ H ₁₄ NO ⁺	[M] ⁺	104.1069	104.1074	4.79	-
69	1.16	Valine	C ₅ H ₁₁ NO ₂	[M+H] ⁺	118.0862	118.0864	1.69	-
70	1.17	Proline	C ₅ H ₁₀ NO ₂	[M+H] ⁺	116.0706	116.0709	2.58	70.0660 [M+H-CH ₂ O ₂] ⁺
71	1.23	Phenylalanine	C ₉ H ₁₁ NO ₂	[M+H] ⁺	166.0862	166.0862	0.00	91.0548 [M+H-C ₂ H ₄ NO ₂] ⁺
72	1.65	Adenosine	C ₁₀ H ₁₃ N ₅ O ₄	[M+H] ⁺	268.1040	268.1040	0.00	136.0620 [M+H-C ₃ H ₈ O ₄] ⁺
73	1.76	Acetophenone	C ₈ H ₈ O	[M+H] ⁺	121.0647	121.0651	3.30	107.0496 [M+H-CH ₂] ⁺
74	3.19	Caffeic acid	C ₉ H ₈ O ₄	[M+H] ⁺	181.0495	181.0497	1.10	163.0391 [M+H-H ₂ O] ⁺ , 135.0442 [M+H-CH ₂ O ₂] ⁺
75	3.20	Danshensu	C ₉ H ₁₀ O ₅	[M+H] ⁺	199.0600	199.0603	1.50	181.0497 [M+H-H ₂ O] ⁺ , 163.0391 [M+H-H ₄ O ₂] ⁺ , 135.0442 [M+H-CH ₄ O ₃] ⁺
76	3.84	protocatechuic acid	C ₇ H ₆ O ₄	[M+H] ⁺	155.0338	155.0339	0.64	137.0235 [M+H-H ₂ O] ⁺ , 127.0393 [M+H-CO] ⁺
77	4.38	Tryptophan	C ₁₁ H ₁₂ N ₂ O ₂	[M+H] ⁺	205.0971	205.0974	1.46	161.1073 [M+H-CO ₂] ⁺ , 144.0810 [M+H-CH ₃ NO ₂] ⁺
78	4.98	Cryptochlorogenic acid	C ₁₆ H ₁₈ O ₉	[M+H] ⁺	355.1023	355.1028	1.40	179.0343 [M+H-C ₇ H ₁₂ O ₅] ⁺ , 163.0392 [M+H-C ₇ H ₁₄ O ₆] ⁺ , 135.0443 [M+H-C ₈ H ₁₄ O ₇] ⁺
79	5.13	Chlorogenic acid	C ₁₆ H ₁₈ O ₉	[M+H] ⁺	355.1023	355.1026	0.84	179.0338 [M+H-C ₇ H ₁₂ O ₅] ⁺ , 163.0391 [M+H-C ₇ H ₁₄ O ₆] ⁺ , 135.0442 [M+H-C ₈ H ₁₄ O ₇] ⁺

80	5.24	Neochlorogenic acid	C ₁₆ H ₁₈ O ₉	[M+H] ⁺	355.1023	355.1029	1.68	179.0339 [M+H-C ₇ H ₁₂ O ₅] ⁺ ,163.0391 [M+H-C ₇ H ₁₄ O ₆] ⁺ 135.0442 [M+H-C ₈ H ₁₄ O ₇] ⁺
81	5.27	Magnocurarine	C ₁₉ H ₂₄ NO ₃ ⁺	[M] ⁺	314.1750	314.1748	-0.63	269.1172 [M-C ₂ H ₇ N] ⁺ ,237.0918 [M-C ₃ H ₁₁ NO] ⁺ ,209.0962 [M-C ₄ H ₁₁ NO ₂] ⁺
82	5.28	3,4-Dihydroxybenz aldehyde	C ₇ H ₆ O ₃	[M+H] ⁺	139.0389	139.0390	0.71	121.0287 [M+H-H ₂ O] ⁺ ,111.0444 [M+H-CO] ⁺
83	5.29	Dihydro-11-hydroxy-stepholidine-glucoside	C ₂₅ H ₃₁ NO ₁₀	[M+H] ⁺	506.2020	506.2026	1.18	344.1494 [M+H-C ₆ H ₁₀ O ₅] ⁺ ,208.0970 [M+H-C ₁₄ H ₁₈ O ₇] ⁺ 190.0864 [M+H-C ₁₄ H ₂₀ O ₈] ⁺
84	5.38	Isoferulic acid	C ₁₀ H ₁₀ O ₄	[M+H] ⁺	195.0651	195.0653	1.53	177.0547 [M+H-H ₂ O] ⁺ ,149.0598 [M+H-CH ₂ O ₂] ⁺
85	5.92	9-O-Berberine glucoside	C ₂₅ H ₂₆ NO ₉ ⁺	[M] ⁺	484.1602	484.1606	0.82	322.1083 [M-C ₆ H ₁₀ O ₅] ⁺ ,308.0924 [M-C ₇ H ₁₀ O ₆] ⁺
86	6.08	Magnoflorine	C ₂₀ H ₂₄ NO ₄ ⁺	[M] ⁺	342.1699	342.1700	0.29	297.1122 [M-C ₂ H ₇ N] ⁺ ,282.0886 [M-C ₃ H ₁₀ N] ⁺ ,265.0860 [M-C ₃ H ₁₁ NO] ⁺ 237.0909 [M-C ₄ H ₁₁ NO ₂] ⁺
87	6.43	11-hydroxy-stepholidine-glucoside	C ₂₅ H ₂₉ NO ₁₀	[M+H] ⁺	504.1864	504.1867	0.59	342.1337 [M+H-C ₆ H ₁₀ O ₅] ⁺ ,205.0814 [M+H-C ₁₄ H ₁₈ O ₇] ⁺ 188.0707 [M+H-C ₁₄ H ₂₀ O ₈] ⁺
88	6.47	Ferulic acid	C ₁₀ H ₁₀ O ₄	[M+H] ⁺	195.0651	195.0653	1.53	177.0547 [M+H-H ₂ O] ⁺ ,149.0598 [M+H-CH ₂ O ₂] ⁺
89	6.61	Magnoflorine glucoside	C ₂₆ H ₃₄ NO ₉ ⁺	[M] ⁺	504.2228	504.2232	0.79	342.1702 [M-C ₆ H ₁₀ O ₅] ⁺ ,297.1120 [M-C ₈ H ₁₇ NO ₅] ⁺
90	6.70	Rosmarinic acid	C ₁₈ H ₁₆ O ₈	[M+H] ⁺	361.0917	361.0917	0.00	181.0494 [M+H-C ₉ H ₈ O ₄] ⁺ ,163.0391 [M+H-C ₉ H ₁₀ O ₅] ⁺ , 135.0442 [M+H-C ₁₀ H ₁₀ O ₆] ⁺
91	6.74	8,9-di-demethyl-epiberberine	C ₁₈ H ₁₄ NO ₄ ⁺	[M] ⁺	308.0917	308.0917	0.00	280.0970 [M-CO] ⁺ ,278.0815 [M-CH ₂ O] ⁺ ,265.0729 [M-C ₂ H ₃ O] ⁺
92	7.08	Dihydro-columbamine/Dihydro-jatro rhizine	C ₂₀ H ₂₂ NO ₄ ⁺	[M] ⁺	340.1543	340.1543	0.00	325.1308 [M-CH ₃] ⁺ ,324.1229 [M-CH ₄] ⁺ ,310.1069 [M-C ₂ H ₆] ⁺ 308.1284 [M-C ₂ H ₈] ⁺ ,280.1331 [M-C ₂ H ₄ O] ⁺

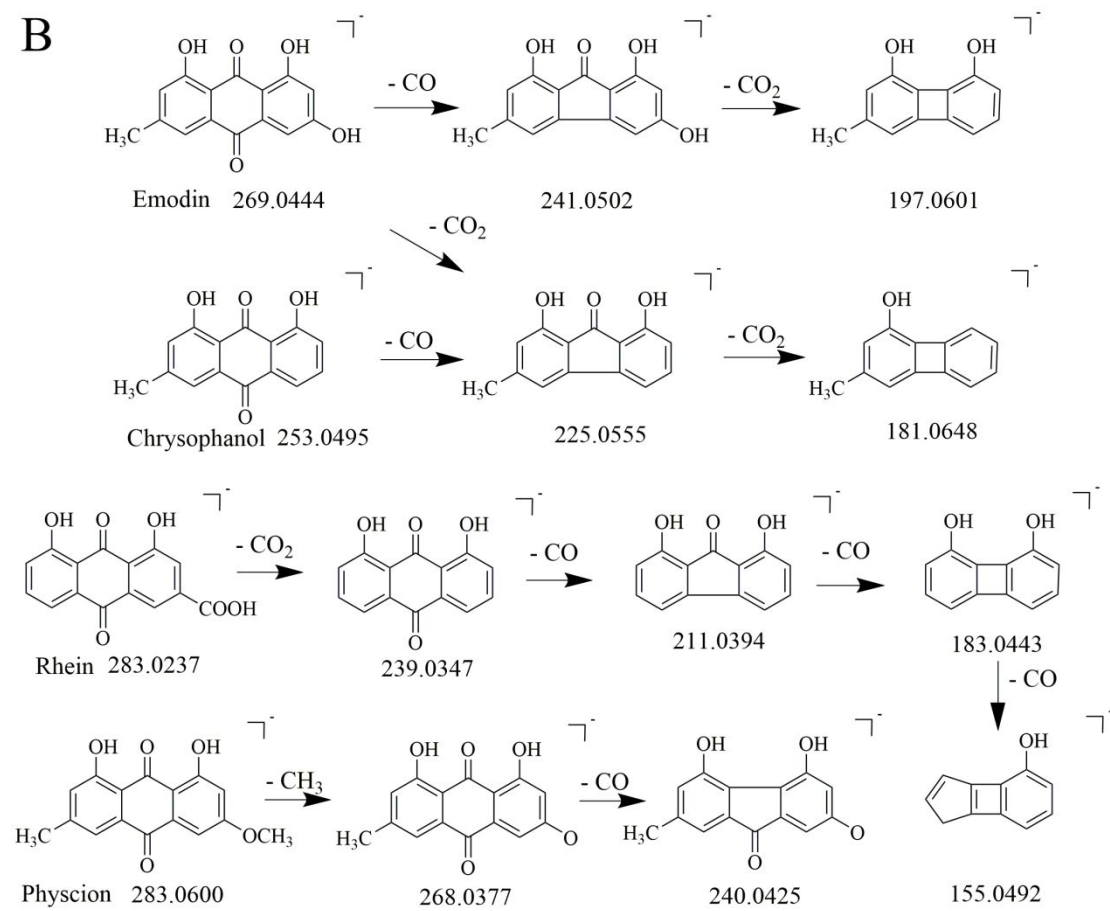
93	7.10	8-Oxocoptisine	C ₁₉ H ₁₃ NO ₅	[M+H] ⁺	336.0866	336.0866	0.00	318.0761 [M+H-H ₂ O] ⁺ ,308.0916 [M+H-CO] ⁺ ,294.0751 [M+H-C ₂ H ₂ O] ⁺ 290.0808 [M+H-CH ₂ O ₂] ⁺
94	7.25	Menisperine	C ₂₁ H ₂₆ NO ₄	[M] ⁺	356.1856	356.1857	0.28	311.1278 [M-C ₂ H ₇ N] ⁺ ,251.1064 [M-C ₄ H ₁₁ NO ₂] ⁺
95	7.35	Demethyleneberberine glucoside	C ₂₅ H ₂₈ NO ₉	[M] ⁺	486.1758	486.1761	0.61	324.1226 [M-C ₆ H ₁₀ O ₅] ⁺ ,308.0912 [M-CH ₄] ⁺
96	7.47	Demethyleneberberine	C ₁₉ H ₁₈ NO ₄ ⁺	[M] ⁺	324.1230	324.1230	0.00	309.0995 [M-CH ₃] ⁺ ,294.0761 [M-C ₂ H ₆] ⁺ ,266.0815 [M-C ₃ H ₆ O] ⁺
97	7.58	Berberrubine	C ₁₉ H ₁₆ NO ₄ ⁺	[M] ⁺	322.1073	322.1073	0.00	307.0839 [M-CH ₃] ⁺ ,294.1124 [M-CO] ⁺
98	7.65	Noroxyhydrastinine	C ₁₀ H ₉ NO ₃	[M+H] ⁺	192.0655	192.0656	0.52	149.0599 [M+H-CONH] ⁺
99	7.75	Groenlandicine	C ₁₉ H ₁₆ NO ₄ ⁺	[M] ⁺	322.1073	322.1074	0.31	307.0839 [M-CH ₃] ⁺ ,294.1120 [M-CO] ⁺
100	7.80	11-hydroxyl-groenlandicine	C ₁₉ H ₁₆ NO ₅ ⁺	[M] ⁺	338.1022	338.1021	-0.29	322.0709 [M-CH ₄] ⁺ ,310.0172 [M-CO] ⁺ ,306.0763 [M-CH ₄ O] ⁺
101	8.00	Oxyepiberberine	C ₂₀ H ₁₇ NO ₅	[M+H] ⁺	352.1179	352.1180	0.28	337.0945 [M+H-CH ₃] ⁺ ,322.0711 [M+H-C ₂ H ₆] ⁺ ,308.0917 [M+H-C ₃ H ₈] ⁺ 294.0745 [M+H-C ₃ H ₆ O] ⁺
102	8.08	Dihydropalmatine	C ₂₁ H ₂₃ NO ₄	[M+H] ⁺	354.1699	354.1693	-1.69	339.1465 [M+H-CH ₃] ⁺ ,338.1385 [M+H-CH ₄] ⁺ ,324.1226 [M+H-C ₂ H ₆] ⁺ 322.1438 [M+H-C ₂ H ₈] ⁺ ,310.0979 [M+H-C ₃ H ₈] ⁺
103	8.55	Columbamine	C ₂₀ H ₂₀ NO ₄ ⁺	[M] ⁺	338.1386	338.1387	0.29	323.1352 [M-CH ₃] ⁺ ,322.1074 [M-CH ₄] ⁺ ,308.0917 [M-C ₂ H ₆] ⁺ 306.1130 [M-C ₂ H ₈] ⁺ ,294.1124 [M-C ₂ H ₄ O] ⁺
104	8.64	Epiberberine	C ₂₀ H ₁₈ NO ₄ ⁺	[M] ⁺	336.1230	336.1229	-0.30	321.0991 [M-CH ₃] ⁺ ,320.0918 [M-CH ₄] ⁺ ,306.0753 [M-C ₂ H ₆] ⁺ 292.0966 [M-C ₂ H ₄ O] ⁺
105	8.69	Jatrorrhizine	C ₂₀ H ₂₀ NO ₄ ⁺	[M] ⁺	338.1386	338.1385	-0.30	323.1352 [M-CH ₃] ⁺ ,322.1073 [M-CH ₄] ⁺ ,308.0916 [M-C ₂ H ₆] ⁺ 306.1127 [M-C ₂ H ₈] ⁺ ,294.1124 [M-C ₂ H ₄ O] ⁺
106	8.75	Coptisine	C ₁₉ H ₁₄ NO ₄ ⁺	[M] ⁺	320.0917	320.0918	0.31	292.0966 [M-CO] ⁺
107	9.23	13-Methylepiberberine	C ₂₁ H ₂₀ NO ₄ ⁺	[M] ⁺	350.1386	350.1387	0.28	335.1153 [M-CH ₃] ⁺ ,334.1073 [M-CH ₄] ⁺ ,306.1121 [M-C ₂ H ₄ O] ⁺

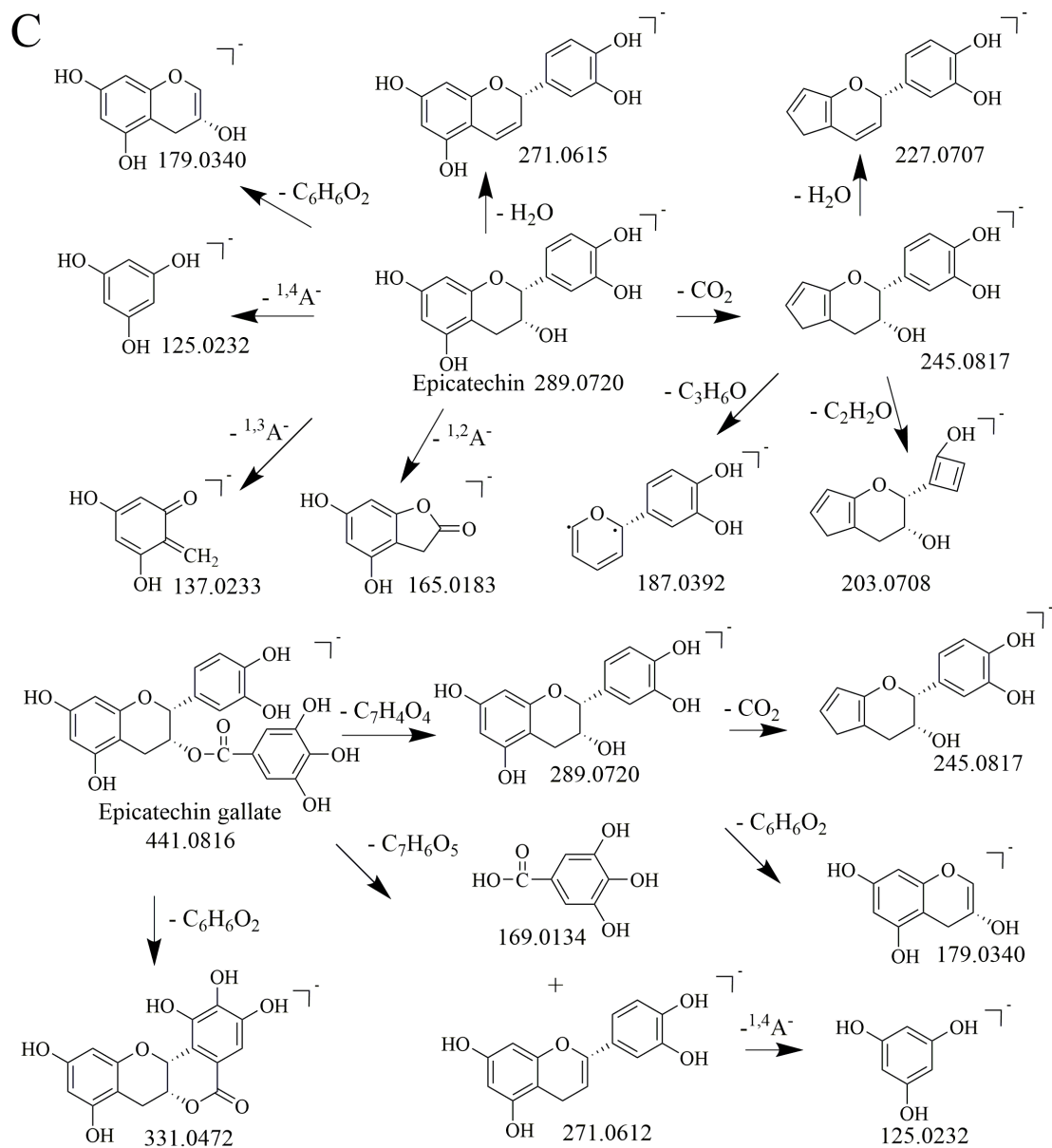
108	9.37	Oxoglaucine	$C_{20}H_{17}NO_5$	$[M+H]^+$	352.1179	352.1174	-1.41	337.0944 $[M+H-CH_3]^+$, 322.0712 $[M+H-C_2H_6]^+$, 320.0919 $[M+H-C_2H_8]^+$ 308.0917 $[M+H-C_3H_8]^+$, 307.0856 $[M+H-C_3H_9]^+$, 294.0760 $[M+H-C_3H_6O]^+$
109	9.44	Worenine	$C_{20}H_{16}NO_4^+$	$[M]^+$	334.1073	334.1073	0.00	319.0843 $[M-CH_3]^+$, 306.1122 $[M-CH_4]^+$
110	9.55	Palmatine	$C_{21}H_{22}NO_4^+$	$[M]^+$	352.1543	352.1542	-0.28	337.1307 $[M-CH_3]^+$, 336.1229 $[M-CH_4]^+$, 322.1074 $[M-C_2H_6]^+$ 308.1281 $[M-C_3H_8]^+$
111	9.67	Berberine	$C_{20}H_{18}NO_4^+$	$[M]^+$	336.1230	336.1230	0.00	321.0997 $[M-CH_3]^+$, 320.0919 $[M-CH_4]^+$, 306.0764 $[M-C_2H_6]^+$ 292.0969 $[M-C_2H_4O]^+$, 278.0805 $[M-C_3H_6O]^+$
112	10.12	Dehydrocorydaline	$C_{22}H_{24}NO_4^+$	$[M]^+$	366.1699	366.1701	0.55	351.1465 $[M-CH_3]^+$, 336.1228 $[M-C_2H_6]^+$, 334.1432 $[M-C_2H_8]^+$ 322.1437 $[M-C_3H_8]^+$
113	10.37	13-Methylberberin e	$C_{21}H_{20}NO_4^+$	$[M]^+$	350.1386	350.1387	0.29	335.1151 $[M-CH_3]^+$, 334.1073 $[M-CH_4]^+$, 320.0916 $[M-C_2H_6]^+$ 306.1125 $[M-C_2H_4O]^+$
114	11.47	Acacetin	$C_{16}H_{12}O_5$	$[M+H]^+$	285.0757	285.0757	0.00	270.0521 $[M+H-CH_3]^+$, 242.0574 $[M+H-C_2H_3O]^+$, 211.0756 $[M+H-C_2H_2O_3]^+$
115	14.81	Oxyberberine	$C_{20}H_{17}NO_5$	$[M+H]^+$	352.1179	352.1180	0.28	337.0945 $[M+H-CH_3]^+$, 322.0712 $[M+H-C_2H_6]^+$, 308.0923 $[M+H-C_3H_8]^+$ 294.0766 $[M+H-C_3H_6O]^+$
116	16.45	Candicine	$C_{11}H_{18}NO^+$	$[M+H]^+$	180.1382	180.1382	0.00	121.0646 $[M+H-C_3H_9N]^+$, 105.0700 $[M+H-C_3H_9NO]^+$
117	17.49	Linoleic acid	$C_{18}H_{32}O_2$	$[M+H]^+$	281.2475	281.2476	0.35	263.2370 $[M+H-H_2O]^+$, 197.1540 $[M+H-C_6H_{12}]^+$
118	19.40	Eleostearic acid	$C_{18}H_{30}O_2$	$[M+H]^+$	279.2318	279.2318	0.00	261.2212 $[M+H-H_2O]^+$, 109.1016 $[M+H-C_{10}H_{18}O_2]^+$
119	25.36	Palmitic acid	$C_{16}H_{32}O_2$	$[M+H]^+$	257.2475	257.2475	0.00	239.2369 $[M+H-H_2O]^+$

A



B





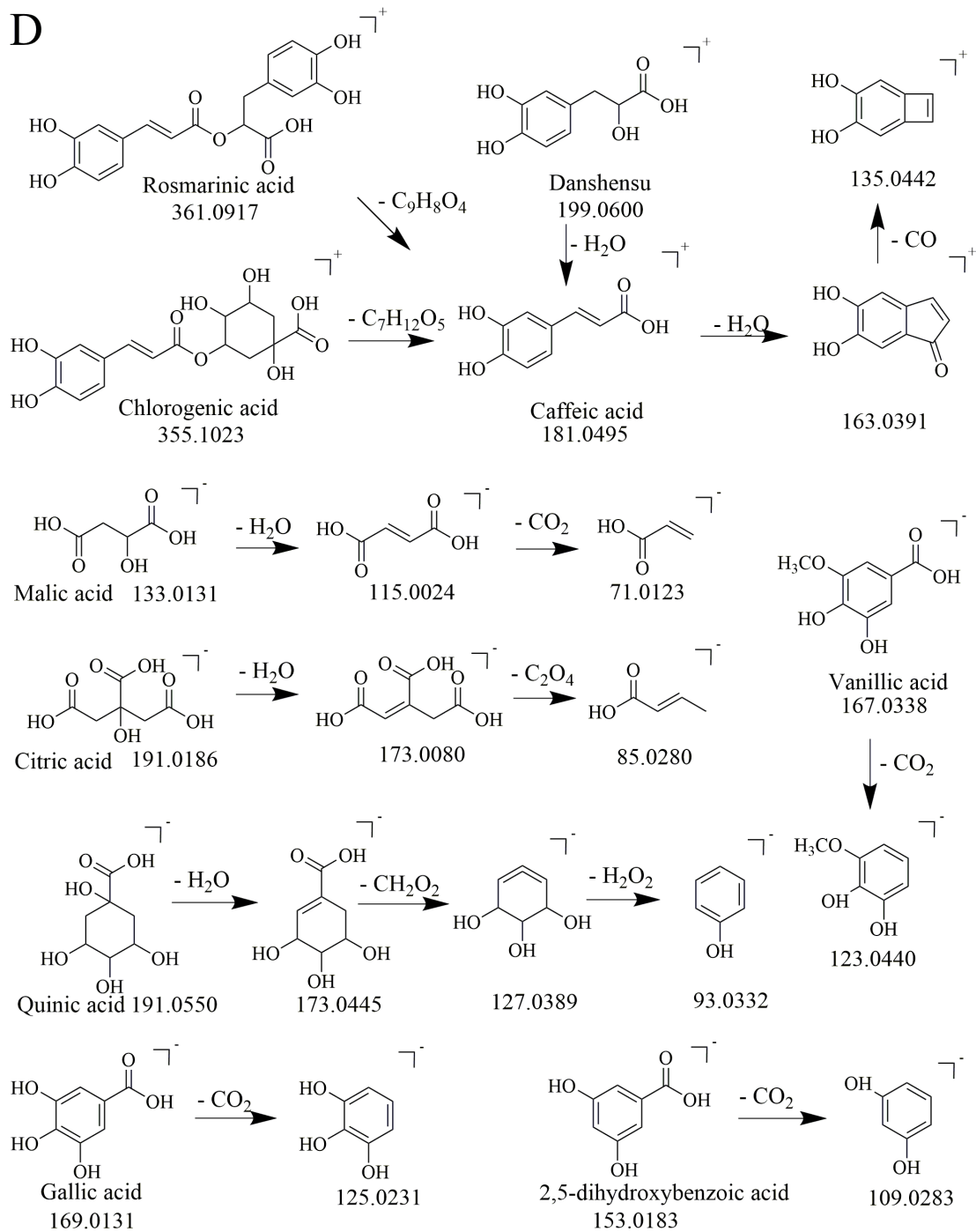


Figure S1. The cracking law of compounds (A) Alkaloids, (B) Anthraquinones, (C) Tannins, (D) Organic acids.